

FISCHER TROPSCH: A FUTURISTIC VIEW

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INTRODUCTION

During the last couple of years there has been a renewed interest in the use of Fischer-Tropsch technology for the conversion of natural gas to liquids. Some of the factors that contributed to this are:

- (i) An increase in the known reserves of natural gas.
- (ii) The need to monetize remote or stranded natural gas.
- (iii) Environmental pressure to minimize the flaring of associated gas.
- (iv) Improvements in the cost-effectiveness of Fischer-Tropsch technology resulting from the development of more active catalysts and improved reactor designs.

The process to convert natural gas to liquids can be divided into three process steps:

- (i) Syngas generation
- (ii) Syngas conversion
- (iii) Hydroprocessing

Although all three of these technologies are well established, individually optimized and commercially proven, the combined use is not widely applied. This poses an interesting challenge to the designer, namely to obtain the most cost-effective combination of these three technologies. In order to make the Gas-to-Liquids (GTL) technology more competitive, the challenge goes beyond the optimization that deals only with the known aspects of these technologies. It also includes those aspects that are not commercialized yet and that may still be in the very early stages of development.

OPTIMIZATION OF EXISTING TECHNOLOGIES

SYNGAS GENERATION

To convert natural gas (mostly methane) to syngas (a mixture of H_2 and CO), the designer can choose from the following four well established reforming technologies:

- (i) Steam reforming
- (ii) Partial oxidation (POX)
- (iii) Autothermal reforming
- (iv) Combined or two-step reforming

The choice of reformer technology will have an influence on the thermal efficiency of the plant as a whole and on the capital costs of the reformer, oxygen plant (where applicable) and the Fischer-Tropsch section. One of the biggest challenges is to optimize the energy integration between the syngas generation and syngas conversion sections.

STEAM REFORMING

An obvious advantage of steam reforming is that it does not need an oxygen plant. However, since steam reformers are more costly than either POX or autothermal reformers, there is a minimum plant size above which the economy of scale of a

cryogenic oxygen plant in combination with a POX or autothermal reformer is cheaper than a steam reformer on its own.

Other disadvantages of steam reforming are:

- (i) Syngas with a H_2/CO ratio (>4) which is much higher than what is optimally needed by the Fischer-Tropsch section.
- (ii) Lower methane conversion due to a maximum operating temperature of below $900\text{ }^{\circ}\text{C}$.
- (iii) The high usage rate of water makes it unsuitable for arid regions.

Recycling of CO_2 and removal of the excess H_2 by means of membranes can lower the H_2/CO ratio to a level acceptable to the Fischer-Tropsch reaction. Since the methane conversion is also a function of the operating pressure, decreasing the operating pressure of the reformer can increase the methane conversion. Due to the costs involved with these steps, it is most likely that steam reforming will only be considered when one or more of the following conditions hold:

- (i) A relative small GTL plant with a capacity of well below 10 000 bpd.
- (ii) The additional H_2 can be used for other applications like methanol or ammonia production.
- (iii) The natural gas has a high CO_2 content.
- (iv) Suitable water can be obtained at a low cost.

PARTIAL OXIDATION REFORMING

The non-catalytic partial combustion of methane produces syngas with a H_2/CO ratio (<2) close to the optimum needed by the Fischer-Tropsch section. This low H_2/CO ratio gas results from the very little, if any, steam that is used in the process. Due to the absence of catalyst, the reformer operates at an exit temperature of about $1400\text{ }^{\circ}\text{C}$. This high temperature and the absence of catalyst have the following disadvantages as compared to an autothermal reformer:

- (i) Formation of soot and much higher levels of ammonia and HCN, which necessitates the use of a scrubber to clean the gas.
- (ii) Higher oxygen consumption.
- (iii) Due to the absence of the water-gas shift reaction, the unconverted methane as well as the methane produced by the Fischer-Tropsch reaction can not be recycled to the reformer without removing the CO_2 from the Fischer-Tropsch tail gas.

Depending on the energy needs of the plant, the syngas from the reformer can either be cooled by means of a water quench or by the production of steam in a heat exchanger. A quench system is the less costly of the two, but is also less thermally efficient. In designing a POX based GTL plant, the choice between a quench or a waste heat reboiler will depend on the relative cost of capital and energy.

AUTOTHERMAL REFORMING

Unlike partial oxidation reforming, autothermal reforming uses a catalyst to reform the natural gas to syngas in the presence of steam and oxygen. Due to the milder operating conditions (exit temperature of $\pm 1\ 000\text{ }^{\circ}\text{C}$) and the use of steam (S/C ratio normally more than 1,3), the syngas is soot free and less ammonia and HCN are produced as compared to a POX. However, at a S/C ratio of 1,3 the syngas will have a H_2/CO ratio of about 2,5, which is higher than the ratio needed by the Fischer-Tropsch section. The H_2/CO ratio can be controlled by a combination of lowering the S/C ratio and recycling the CO_2 to the reformer. Although S/C ratios below 1,3 are not commercially used, Haldor Topsøe and Sasol have successfully completed low S/C ratio tests on a commercial scale at Sasol's synfuels plant in South Africa.

Some of the other design parameters of the syngas section that influence the cost and thermal efficiency of the GTL plant are:

- (i) The preheat temperatures of oxygen and natural gas. The higher these temperatures are, the less oxygen will be used. The maximum preheat temperatures are determined by safety factors and by the need to prevent soot formation.

- (ii) The pressure of the steam generated in the waste heat reboiler. The higher the steam-pressure, the more efficient energy can be recovered from the steam, but the more costly the steam and boiler feed water treatment systems become. The optimum steam pressure will be determined by the relative cost of capital and energy.

COMBINED REFORMING

By combining a steam reformer with an autothermal reformer, better energy utilization can be obtained than with either steam or autothermal reforming alone. Depending on the degree of energy integration and the specific operating conditions, the thermal efficiency of the GTL plant can be improved by about 1 to 2 percentage points. Although less expensive than steam reforming on its own, this type of reforming is more expensive than autothermal reforming and the choice between combined and autothermal reforming will depend on the cost of the natural gas.

SYNGAS CONVERSION

Due to its high activity and long life, cobalt-based Fischer-Tropsch catalyst is currently the catalyst of choice for the conversion of syngas to liquid fuels. The exothermic nature of the Fischer-Tropsch reaction combined with the high activity of the Co catalyst makes the removal of heat from the reactor of critical importance. In the case of a tubular fixed bed reactor, this becomes even more problematic due to the inherent temperature profiles inside the tube. This problem can be controlled by finding the balance between the tube diameter and the usage of a "quench" medium such as the recycle of inerts.

Due to the good mixing and heat transfer characteristics of a slurry phase reactor, the temperature control in such a reactor is much less of a problem than in a tubular fixed bed reactor. Care must however be taken in the design of such a reactor that, during normal operating conditions and also during the shutdown of the reactor, no stagnant zones with poor mixing occur which may result in localized hot spots. If the catalyst is exposed to too high a temperature, carbon will be formed, which may damage the structural integrity of the catalyst.

Another critical design aspect of a slurry phase reactor is the separation of the catalyst from the wax. Sasol was successful in the development of a very efficient catalyst/wax separation system. By matching the characteristics of the catalyst with those of the separation system, the loss of catalyst can be restricted to a few ppm of catalyst in the wax produced by the Fischer-Tropsch process.

Since the H_2/CO ratio of the syngas is an important design variable to maximize the production of high quality diesel, the designs of the reformer and the Fischer-Tropsch sections can not be done in isolation. The most cost effective design for both units can only be obtained by taking the mutual interaction between these units into account.

HYDROPROCESSING

The wax and hydrocarbon condensate produced by the Fischer-Tropsch process is predominantly linear paraffins with a small fraction of olefins and oxygenates. The hydrogenation of the olefins and oxygenates and the hydrocracking of the wax to naphtha and diesel can be done at relatively mild conditions.

In the design of the hydrocracker, a balance must be found between the per-pass conversion, diesel selectivity and diesel properties. The higher the per-pass conversion, the smaller the cracker will be due to the lesser recycle of material back to the cracker. This will however be at the expense of the diesel selectivity, since over cracking of the liquid to gasses will occur. Another complicating factor is that the per-pass conversion also influences the diesel quality. The higher the per-pass conversion, the better the cold flow properties but the lower the cetane value will be, due to the increased degree of isomerisation.

CAPITAL AND OPERATING COSTS

CAPITAL COST

Studies done by Sasol indicated that the total installed cost of a two train 30 000 barrel per day GTL plant is in the order of about \$24 000 per daily barrel. It is also believed that the capital cost can be further decreased to about \$20 000 per daily barrel by:

- (i) The economy of scale of larger single train capacity plants.
- (ii) The economy of scale of adding trains.
- (iii) Improved process integration and optimization.
- (iv) Progressing up the learning curve.

The capital cost associated with the syngas generation section is more than 50% of the total IBL cost of the plant.

OPERATING COST

Based on a gas cost of \$0,5 per MM BTU, the estimated operating cost is in the order of about \$10 per barrel of which the gas cost is \$5 per barrel. The main areas of energy loss from the process are the syngas generation and syngas conversion sections. The oxygen plant and reformer combination is responsible for about 45% and the Fischer-Tropsch section for about 50% of the energy losses from the plant.

About 50% of energy loss from the Fischer-Tropsch plant is due to condensing of the reaction water produced by the Fischer-Tropsch reaction and the balance results from the inefficiency with which energy is recovered from the relatively low pressure steam.

FUTURE IMPROVEMENTS

In order to have the greatest impact on the economics of the process, future breakthroughs should be in areas that decrease the capitals cost of syngas generation and/or improve the thermal efficiency of the plant as a whole.

An obvious way of improving the thermal efficiency of the process is to combine it with a power generation plant. Such a combination will create a more efficient utilization of the low pressure steam produced by the Fischer-Tropsch process. If the energy associated with this steam is sold at the same price as that of the natural gas (\$0,5 per MM BTU), an additional income of about \$0,5 per barrel can be obtained.

Some of the changes to the reforming section that can increase the thermal efficiency of the process are:

- (i) The use of a heat exchange reformer in combination with an autothermal reformer.
- (ii) The use of a feed/product heat exchanger to recover energy from the reformer outlet.

HEAT EXCHANGE REFORMING

The combination of a heat exchange reformer with an autothermal reformer is very similar to combined reforming, the major difference being that the energy to the steam reformer is not supplied by a fired heater but by the exit gas from the autothermal reformer.

The potential benefits of such a reforming configuration are:

- (i) Savings of about 30% in oxygen consumption.
- (ii) An increase of about 4 percentage points in the thermal efficiency of the plant.

One of the technical issues that must be solved is the potential problem of metal dusting in the heat exchange reformer.

FEED/PRODUCT HEAT EXCHANGE

The oxygen consumption can be decreased by about 3,5% and the production of liquid fuels can be increased by about 2,5% if a feed/product heat exchanger is used to

preheat the natural gas to the reformer. As in the case of heat exchange reforming, metal dusting is also one of the major technical problems that would have to be solved.

OXYGEN TRANSFER MEMBRANES

Another way of eliminating the oxygen plant is to use ceramic membranes to separate the oxygen from the air. In addition to the capital cost savings associated with the elimination of an oxygen plant, the thermal efficiency of the plant can also be improved by combining the oxygen removal and reforming sections into one unit. Early indications are that this technology should significantly reduce the capital cost of the syngas generation section of the GTL plant.

Some of the technical issues that are being researched include the maximization of the oxygen flux and the mechanical strength of the ceramic tubes.

OTHER POTENTIAL IMPROVEMENTS

The Co catalyst can be improved by:

- (i) Increasing the catalyst life by making it more resistant to irreversible sulphur poisoning.
- (ii) Changing the selectivity dependency on the H_2/CO ratio to such an extent that high diesel yields can be obtained at H_2/CO ratios similar to the usage ratio. The advantage of such a catalyst would be that, due to the increase in reaction rate at higher H_2/CO ratios, much less catalyst would be needed for the same conversion. To obtain the same conversions at H_2/CO ratio's of 2 and 1,6, 50% more catalyst is needed at the lower H_2/CO ratio.

CONCLUSIONS

Although the three main processing steps of a GTL plant have been individually optimized for other applications, opportunities do exist to decrease the capital and operating costs by re-optimizing these processing steps for GTL applications. In addition to these optimization opportunities, there are other potential breakthroughs that can also significantly reduce the operating and capital costs of a GTL plant.